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"Additive" cooperativity of hydrogen bonds in complexes of catechol with proto acceptors in the gas phase: FTIR spectroscopy and quantum chemical calculation

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ABSTRACT

Experimental study of hydrogen bond cooperativity in hetero-complexes in the gas phase was carr out by IR-spectroscopy method. Stretching vibration frequencies of O—H groups in phenol and catec molecules as well as of their complexes with nitriles and ethers were determined in the gas phase usin specially designed cell. O—H groups experimental frequency shifts in the complexes of catechol induc by the formation of intermolecular hydrogen bonds are significantly higher than in the complexes phenol due to the hydrogen bond cooperativity. It was shown that the cooperativity factors of hydrog bonds in the complexes of catechol with nitriles and ethers in the gas phase are approximately the sa Quantum chemical calculations of the studied systems have been performed using density functio theory (DFT) methods. It was shown, that theoretically obtained cooperativity factors of hydrogen bo in the complexes of catechol with proton acceptors are in good agreement with experimental valu Cooperative effects lead to a strengthening of intermolecular hydrogen bonds in the complexes of catec on about 30%, despite the significant difference in the proton acceptor ability of the bases. The analy within quantum theory of atoms in molecules was carried out for the explanation of this fact.

1. Introduction

Among all types of non-covalent interactions, formed in organic molecules, hydrogen bonds have the greatest impact on their properties and reactivity [1–3]. Cooperativity is an important property of hydrogen bonds. The cooperativity means strengthening or weakening of the hydrogen bonds in the complexes with the adjacent hydrogen bonds in comparison with the binary complexes with a single one [2,4–6]. Cooperativity of hydrogen bonds determines the structure and properties of self-associated solvents (water, alcohols, amides, etc.) [7–10]. In addition, cooperative effect of H-bonding leads to additional stabilization of supramolecular architectures [11,12], proteins and nucleic acids [13,14].One of the most suitable methods to study the cooperativity of hydrogen bonds is IR spectroscopy. This method was used for the investigation of cooperative effects in multi-particle complexes formed in solution [15] and in the inert gas matrices [16]. Study of the cooperative effects in condensed matter is complicated by the presence of various types of non-covalent interactions and the solvent effects [17]. Therefore, investigation of hydrogen bonds cooperativity in the gas phase is of great interest. These studies can give the opportunity to quantify "neat" cooperative effect and to understand the nature of H-bond cooperativity phenomenon. Experimentally t cooperative hydrogen bonds in the gas phase were studied only clusters of aliphatic alcohols and water. The main results of the investigations were reviewed in [18]. The authors [18,19] using spectroscopy method showed that the strength of hydrogen bon in clusters of alcohols and water is much greater than in dime Experimental studies of the hydrogen bond cooperativity in co plexes consisting of different molecules were not carried out in t gas phase. In the last decade, the cooperativity of hydrogen bon in the gas phase was mostly studied using various quantum che ical approaches. Theoretical calculations provide an opportun to study systems with cooperative hydrogen bonds, consisting different number of molecules, which are very difficult to stu experimentally. Hydrogen bond cooperativity in clusters of amid [6,20], some biological molecules [21] and in systems with mul ple unusual weak hydrogen bonds [22] was studied using differe quantum-chemical methods. Authors [23] also used quantum th ory of atoms in molecules (QTAIM) approaches for analysis this phenomenon. In works [24,25] calculations of intramolecu hydrogen bond cooperativity were carried out. Despite significa progress in the use of theoretical calculations, experimental stud of hydrogen bond cooperativity in the gas phase are rather poo distributed.

In this work, we have carried out the experimental study hydrogen bond cooperativity in the gas phase using the infra spectroscopy method. It is quite difficult task to determine spect

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